Energy Storage Research Group (ESRG)
Department of Materials Science and Engineering

Self-Forming Thin Interphases and Electrodes Enabling 3-D Structured High Energy Density Batteries

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Project ID: BAT323

Overview

Timeline

- *Start Date*: October 01, 2016
- *End Date:* September 30, 2019
- **52% complete** as of April 1, 2018

Budget

- Total: $1,271,165
- FY17 DOE : $425,196
- FY18 DOE : $317,544
- 15% Cost Share

Partners

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Barriers/Targets

- *Performance:* Energy densities need to be improved to achieve weight and volume targets; 350 Wh/kg and 750 Wh/L at a cell level
- Safety: Abuse tolerance need to be improved under routine and extreme operating conditions
- *Cost:* Cost currently too high; target is a decrease by factor 3

Relevance: Objectives

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Overall Objectives:

- Develop and implement a novel in-situ formed lithium metal-based metal fluoride battery
- Enable packaged 10 mAh batteries of energy densities > 1000 Wh/L and > 400 Wh/kg at 12V within one planar unit

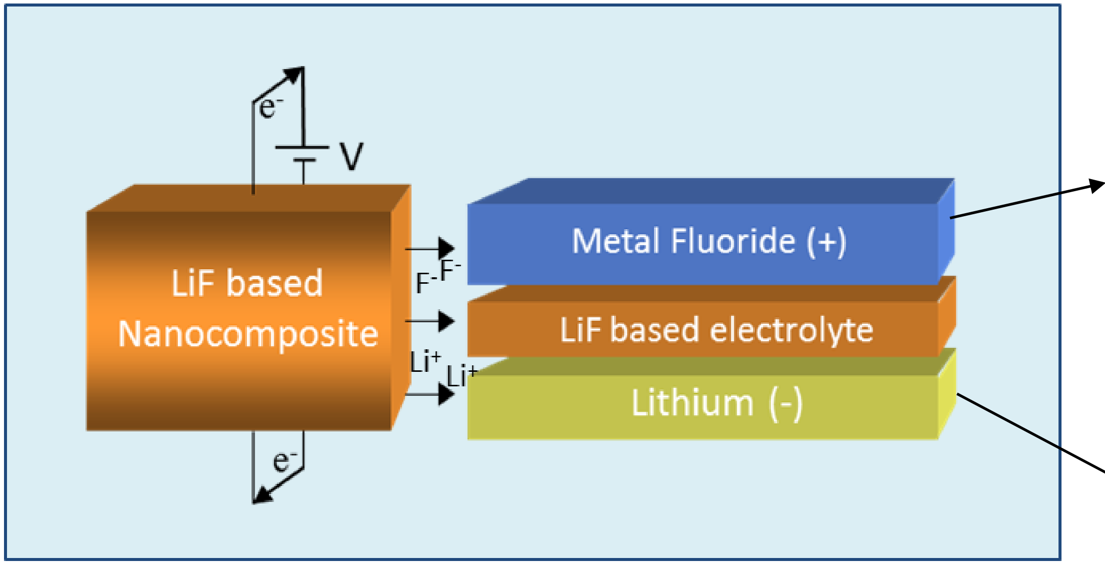
Current Period Objectives:

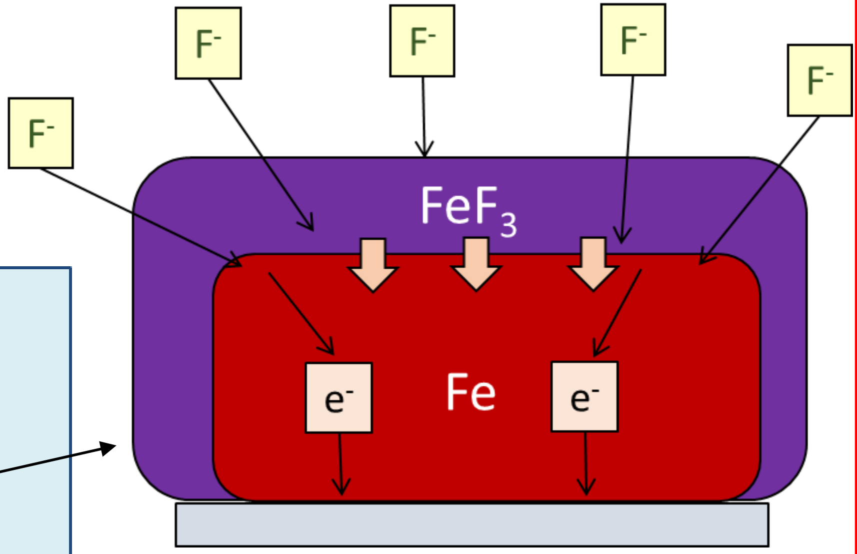
- Achieve > 50% utilization of the initial amount of the positive reactive current collector during in-situ formation of the cell
- Establish a bi-ion conductive glass composition with ionic conductivity of > $1x10^{-4}$ *post* in-situ formation
- Achieve self-formed cell stack with energy densities > 500 Wh/L and 200 Wh/kg at a rate of at least C/10

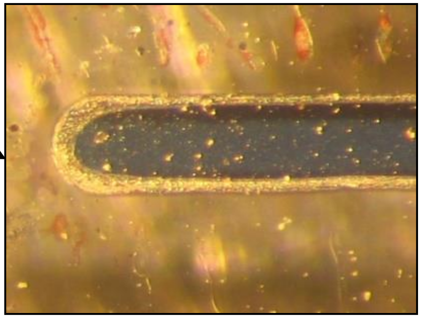
Relevance: Project Impacts Towards DOE's Goals

- ***Performance:*** Highest practical energy density electrochemical system, above DOE-VT Office's targets
- ***Performance:*** Unique pathway to high voltage system enabling high energy density packaged cells, above DOE-VT Office's targets
- ***Performance & Safety:*** Non-flammable solid state electrolytes, would reduce abuse tolerance during shipping and operation
- ***Safety & Cost:*** Eliminate Li metal in fabrication and handling of cells, would improve shipping safety and reduce shipping and fabrication costs
- ***Cost:*** Mask-less, scalable patterning technique with potential for high throughput and low material loss fabrication would reduce costs of complex architecture fabrication
- ***Cost:*** Low cost materials

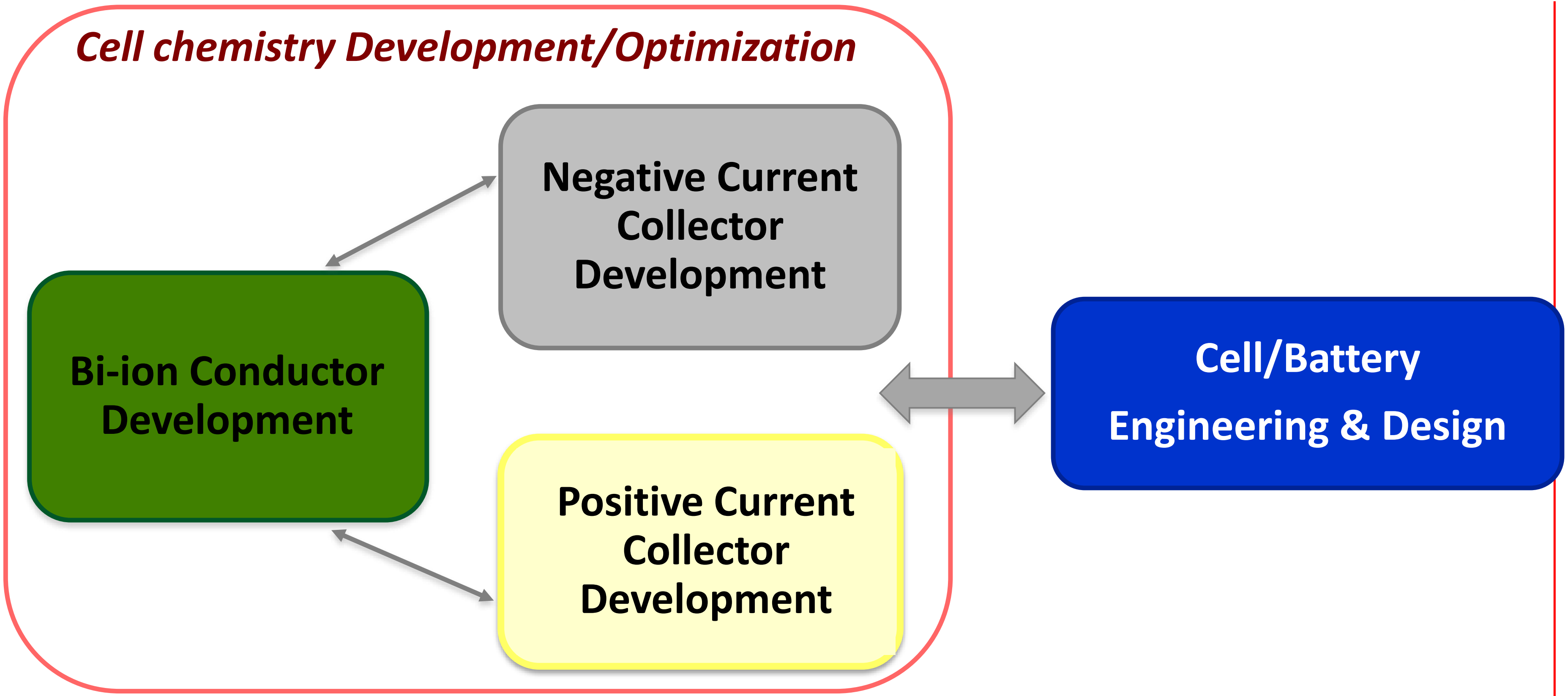
Electrolytically Form
a Solid State Rechargeable Battery
From a Bi-ion Li-F-based Conductor







Approach



- *Positive reactive current collector development:* address composition and scalable fabrication approach
- *Negative reactive current collector development:* address composition and microstructure to facilitate rapid and uniform lithium deposition during the formation cycle and subsequent cycling
- *Bi-ion solid-state conductor development:* address LiF-based composition to enable facile electrolytic decomposition at the interface that will release the F^- and Li+ ions to react with the positive and negative current collectors respectively thereby forming the cell in-situ, while maintaining fast ionic conductor of Li^+ to facilitate subsequent cycles

Approach: FY18 Schedule and Challenges

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- *Challenges to be achieved by the end of FY18*

Milestone	Type	Description	
Negative reactive current collector development	Technical	Establish negative current collector compositions that enable high efficiency of lithium plating and stripping in excess of 90% during the in-situ formation step and >95% during subsequent cycles.	Achieved > 90% during *in-situ* formation In FY17
Bi-ion solid state conductor development	Technical	Establish optimal type and composition of bi-ion conductors that achieves ionic conductivities in excess of 1×10^{-4} S/cm *after* in-situ formation as opposed to the *prior* in-situ formation focus in milestone 1.1.3.1.	✓ Completed FY17 Q1
Design & Fabrication; Electrodes and Cells	Technical	Establish cell stack design that achieves 75% utilization of the positive reactive current collector and 12V	Achieved Utilization > 60%
Cell Stack Performance	Go/No Go	Achieve self-formed cell stack with energy densities of at least 1000 Wh/L and 300 Wh/kg at a rate of C/10, output voltage of 12V, and >80% capacity retention after 100 cycles.	

Approach: FY19 Schedule and Challenges

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- ***Challenges to be achieved by the end of FY19***

Milestone	Type	Description
Positive current collector development	Technical	Establish positive current collector compositions that achieve 90% of the theoretical energy density based on complete utilization of the initial amount of the positive reactive current collector.
Negative current collector development	Technical	Establish negative current collector compositions that enable high efficiency of lithium plating and stripping in excess of 95% during the in-situ formation step and >99% during subsequent cycles.
Bi-ion conductor development	Technical	Achieve <30% increase in electrolyte impedance after 50 cycles as characterized by Electrochemical Impedance Spectroscopy
Design and Fabrication; Electrodes and Cells	Technical	Design and fabricate 10 mAh cell stack that achieves 12V and delivers energy densities of 1400Wh/L and 600 Wh/kg per cell stack.

Approach: Go/No Go Decisions and Final Goals

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FY17 Goal has been slightly modified as per our Continuation Application

FY17

- *In-situ formed cell stack of > 500 Wh/L and 200 Wh/kg at C/10*

Go/ No Go

570 Wh/L achieved in FY17

FY18

- In-situ formed cell stack of > 1000 Wh/L and 300 Wh/kg at C/10
- >80% capacity retention over 100 cycles
- 12V output

Go/ No Go

FY19

- In-situ formed cell stack of > 1400 Wh/L and 600 Wh/kg at C/10
- >80% capacity retention over 300 cycles
- 12V output

Deliverables

- 12 packaged cells of 10 mAh capacity
- Packaged cell: >1000 Wh/L and >400 Wh/kg, and 12V output

Key Technical Accomplishments: Transport/Utilization

Addressing transport barriers in positive electrode to optimize utilization and discharge rate through:

✓ Hybridization of transport pathways:

➔ *Enabled current density improvement by one order of magnitude leading to > C/10 discharge rates*

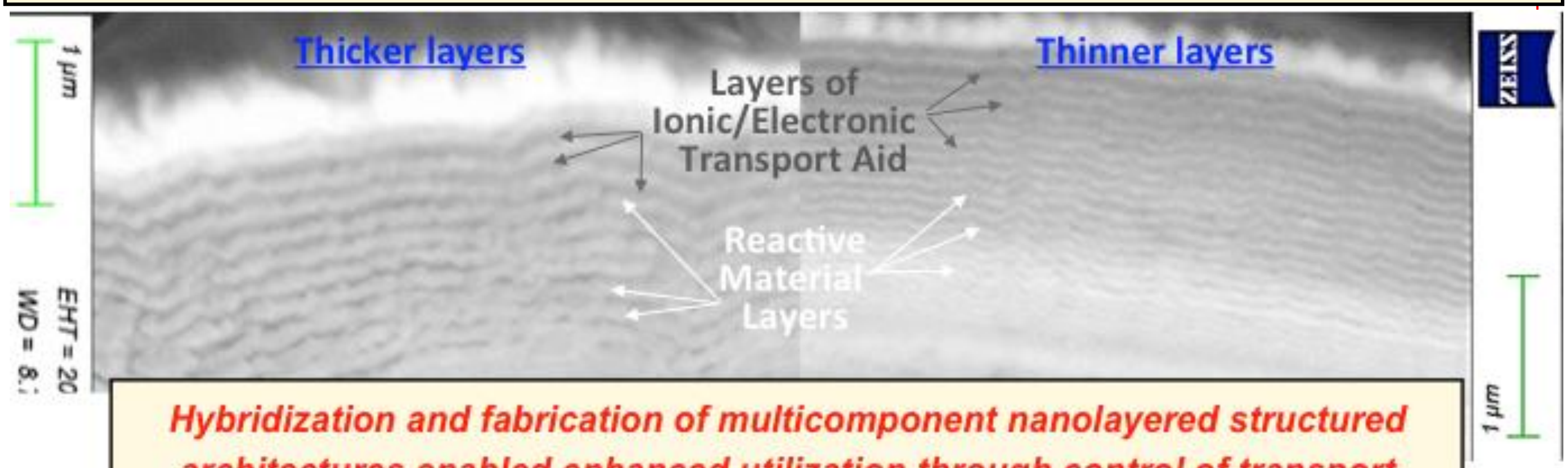
✓ Design and fabrication of multicomponent nanolayered structured architectures:

- Enabled tailoring of the type of conductivity (electronic vs. ionic) through change in chemistry
- Enabled control of the amount of transport pathways

➔ *Resulted in utilization improvement > 60%*

✓ Development of a unique deposition system for the fabrication of these nanolayered architectures:

- Enabled the isolation, characterization, and optimization of positive and negative electrodes
- Enabled high throughput allowing accelerated development
- Enabled user control to fabricate unique compositions
- Is low cost



Hybridization and fabrication of multicomponent nanolayered structured architectures enabled enhanced utilization through control of transport

Key Technical Accomplishments: Transport

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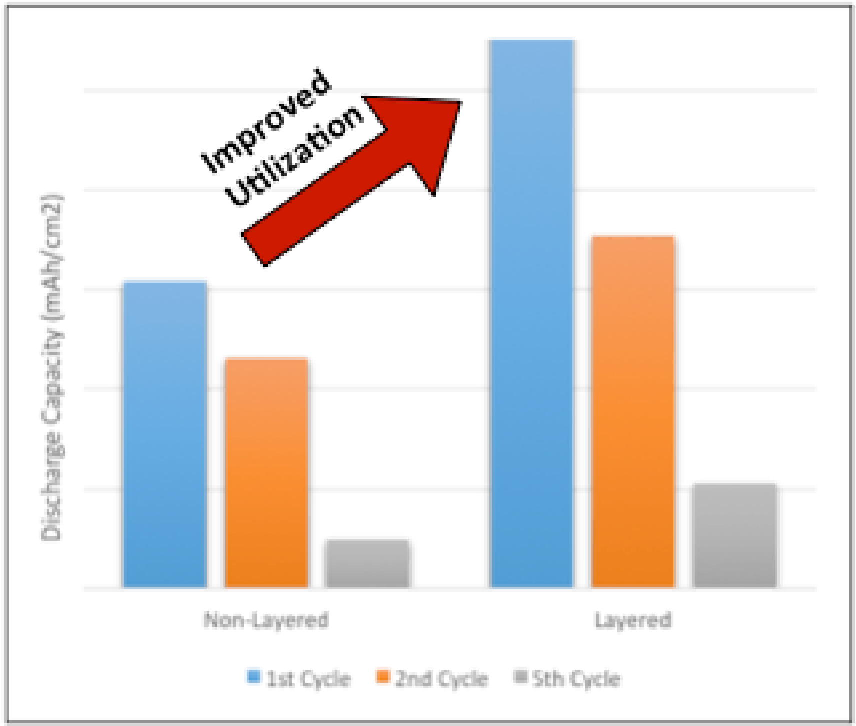
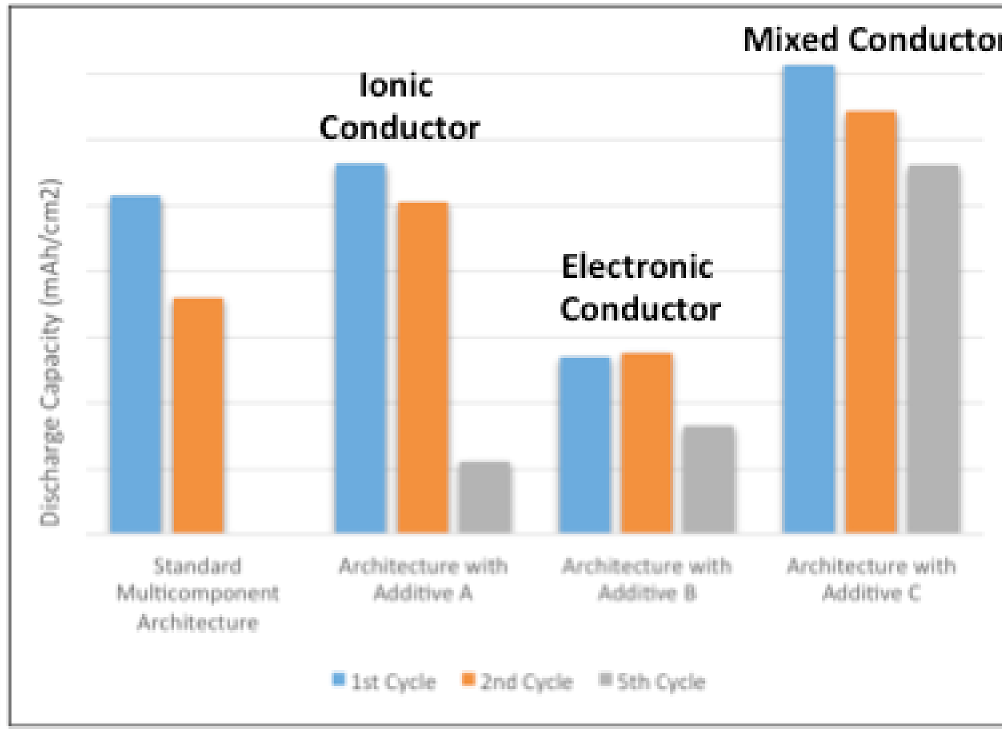
•***Addressing transport barriers in positive electrode to optimize utilization and energy density:***

✓ Nanolayered structured architectures show higher capacity and improved initial capacity retention compared to non-layered structures most likely rooted in its high interface design

✓ Transport tailoring through chemistry change of the nanolayered structured architecture revealed:

- Ionic conductivity increased capacity retention
- Electronic conductivity showed stable retention but decreased capacity
- Mixed conductivity improved both capacity and capacity retention





Mixed conductivity is needed to improve performance including capacity and cycle life

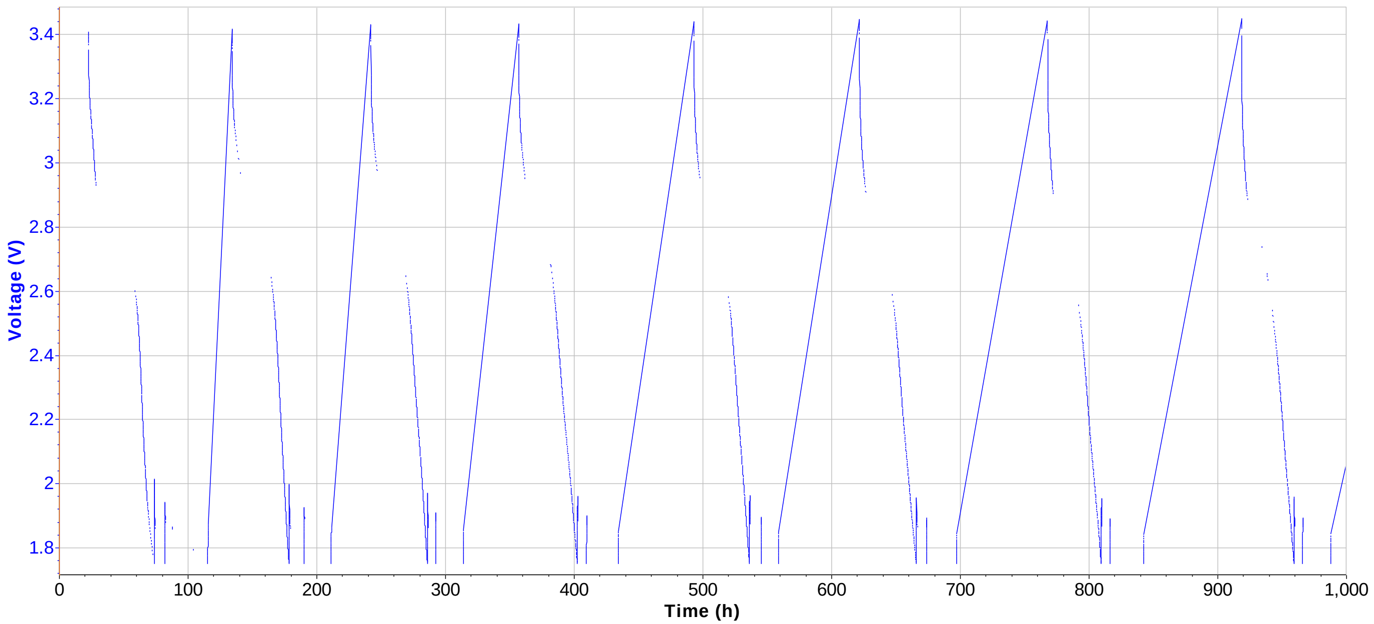
Key Technical Accomplishments:

From Q2 FY17 (AMR 2017)

- ✓ ***Increased energy density from 25 to > 570 Wh/L***
- ✓ ***Improved positive reactive current collector utilization from 1% to > 60 %***
- ✓ ***Rates in the C/2-C/20 range, two orders of magnitude increase***
- ✓ ***Areal capacities approaching 0.4 mAh/cm^2, a factor of 2 increase***
- ✓ ***Improved capacity retention***

•*Discharge voltage profile of hybrid cell design formed in-situ under constant voltage at 3.5V*

Discharge under signature protocol down to 1.75V and charge under constant voltage of 3.5V



Key Technical Accomplishments: Scalable Processing

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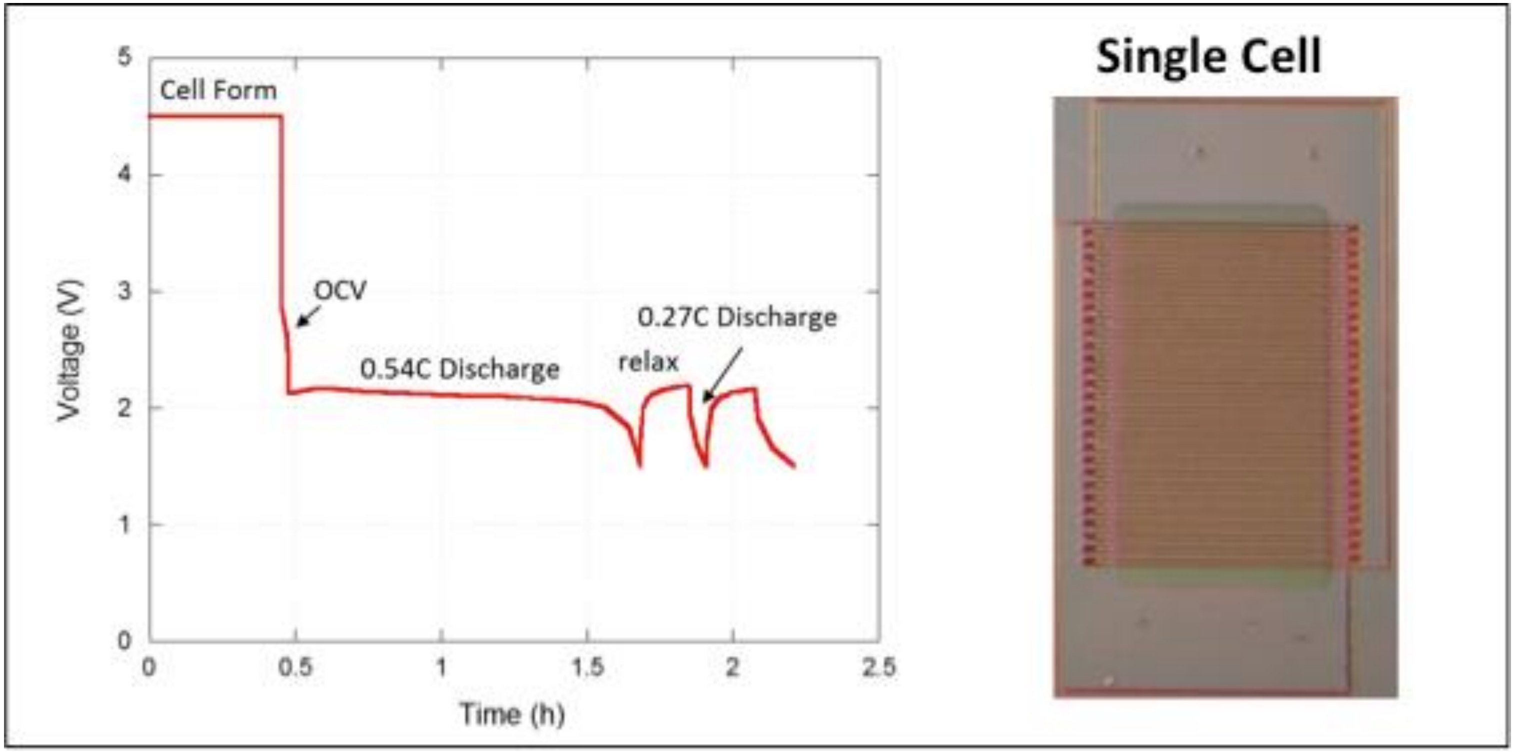
- ***Chemistry & concept applied to scalable manufacturing design:***
  - ✓ Chemistries can be transferred from smaller scale process demonstrated herein
  - ✓ Nanolayered structured architectures can be fabricated
  - ✓ Mass production via continuous roll to roll processing
  - ✓ Cost effective



Chemistries & nanolayered structured architectures can be developed into cost effective mass fabrication process

Responses to Last Year Reviewers' Comments

- Project commenced in October 2016
- Project not reviewed in 2017

Collaborations

- All work has been performed at Rutgers University

Remaining Challenges and Barriers

Negative Current Collector	• Efficiency and reversibility of lithium metal deposition and stripping at the negative current collector • Stability upon cycling
Cell Stability	• Mechanical stability of the cell upon cycling
Cell Design	• Design and optimization of cell architecture to provide 12V in a single planar unit

These issues will be addressed in the future work

Proposed Future Research

Negative Current Collector	• Optimize compositions and microstructures to enable high efficiency Li stripping and plating
Cell Utilization	• Continue the optimization of the cell composition and microstructure to continue improving the cell utilization during in-situ formation of the initial amount of reactive current collector
Cell Stability	• Optimize compositions and microstructures to prevent interfacial impedance growth upon cycling • Identify failure modes and optimize materials to achieve long cycle life
Cell Design	• Design and optimize cell-architecture to provide 12V in a single planar unit

Summary

- ✓ Improvement of the cell electrochemical performance over the past year:
  - Energy density surpassed the FY17 go/no go goal of 500 Wh/L to achieve > 570 Wh/L
  - Areal capacities increased by a factor of two to 0.4 mAh/cm^2
  - Positive reactive current collector utilization improved to > 60 %
  - Rates increased two orders of magnitude to reach C/2-C/20 range
  - Improved capacity retention

- ✓ Improvement of transport within the bulk structure ➔ Enhanced utilization/capacity/capacity retention:
  - Isolation, evaluation and identification of transport limitation processes
  - Hybridization of transport pathways enabled current density increase
  - Multicomponent nanolayered structured architectures enhanced utilization/capacity vs. non-layered bulk structures
  - Mixed conductivity improved utilization/capacity and subsequent capacity retention vs. pure ionic or electronic conductivity of the nanolayered structures

Summary

✓ Development of unique deposition process for the fabrication of versatile multicomponent nanolayered structured architectures

- Manufacture friendly, high flux capable, little waste, cost effective process
- Enabled fine control of the layers thicknesses and relative thicknesses
- Enabled control of the multicomponents chemistries

➔ Enabled control of conductivity type and amount of transport pathways

➔ Enabled adjustment of the cell performance

✓ Development of scalable manufacturing process

- Mass production via continuous roll to roll processing
- Transferrable chemistries and nanolayered architectures demonstrated at smaller scale
- Cost effective

Research conducted in the past year did not encounter unforeseen barriers and the project is on track to achieve the proposed goals